6. COMBUSTION SOURCES OF CDD/CDF: MINIMALLY CONTROLLED AND UNCONTROLLED COMBUSTION SOURCES*

6.1. COMBUSTION OF LANDFILL GAS

The U.S. EPA promulgated emission standards and guidelines in 1996 to control emissions of landfill gas from existing and future landfills under the Clean Air Act (Federal Register, 1996a). Those regulations require the largest landfills in the United States (approximately 312) (i.e., largest on the basis of design capacity) to periodically measure and determine their annual emissions of landfill gas. Landfills that emit annually more than 50 metric tons of nonmethane organic compounds (NMOC) must collect landfill gas and reduce its NMOC content by 98 percent weight through use of a control device. EPA estimates that, when implemented, these controls will reduce NMOC annual emissions from existing landfills by 77,600 metric tons. The cost analysis supporting this rulemaking based control device costs on open flares, because flares are applicable to all the regulated facilities. Assuming that this mass reduction is achieved by use of flares, the corresponding volume of landfill gas that will be burned is approximately 14 billion m^3/yr. The calculation is based on an assumed default NMOC concentration in landfill gas of 1,532 ppmv and a conversion factor of 3.545 mg/m^3 of NMOC per 1 ppmv of NMOC (Federal Register, 1993d). EPA estimated that more than 100 of the approximately 312 landfills had some form of collection or control system, or both, in place in 1991 (Federal Register, 1991b). Thus, a rough approximation of the volume of landfill gas that is currently combusted is 4.7 billion m^3/yr (or 33 percent of the future expected 14 billion m^3/yr reduction). This estimate is similar to the 2.0 to 4.0 billion m^3 of landfill gas that were estimated in EIA (1994) as collected and consumed for energy recovery purposes in 1992. The Energy Information Administration (EIA, 1992) estimated that between 0.9 and 1.8 billion m^3 of landfill gas were collected and burned in 1990 for energy recovery purposes.

Although no data could be located on the levels of CDD/CDFs in untreated landfill gas, several studies have reported detecting CDD/CDFs in the emissions resulting from the

* This chapter discusses combustion sources of CDD/CDF that have some (in the case of combustion of landfill gas) or no post-combustion pollution control equipment for conventional pollutant emissions. Note that very few of the CDD/CDF sources listed in this report control specifically for CDD/CDF emissions.

combustion of landfill gas. Only one study of CDD/CDF emissions from a landfill flare has been reported for a U.S. landfill (CARB, 1990d). The I-TEQ_{DF} and TEQ_{DF}-WHO_{98} emission factor calculated from the results of this study is approximately 2.4 ng TEQ/m^3 of landfill gas combusted. The congener-specific results of this study are presented in Table 6-1. Figure 6-1 presents the CDD/CDF congener emission profile based on these emission factors. Bremmer et al. (1994) reported a lower emission factor, 0.4 ng I-TEQ_{DF}/m^3, from the incineration of untreated landfill gas in a flare at a facility located in The Netherlands. No congener-specific emission factors were provided in Bremmer et al. (1994). The average TEQ emission factor for the CARB (1990d) and Bremmer et al. (1994) studies is 1.4 ng I-TEQ_{DF}/m^3 of landfill gas combusted. Umweltbundesamt (1996) reported even lower TEQ emission factors for landfill gas burned in engines or boiler mufflers rather than in a flare. The reported results for 30 engines and mufflers tested in Germany ranged from 0.001 to 0.28 ng I-TEQ_{DF}/m^3 with most values below 0.1 ng I-TEQ_{DF}/m^3. However, Bremmer et al. (1994) also reported an emission factor of 0.5 ng I-TEQ_{DF}/m^3 from a landfill gas–fired engine in The Netherlands.

The limited emission factor data that are available were judged inadequate for developing national emission estimates that could be included in the national inventory. However, a preliminary estimate of the potential annual TEQ release from landfills can be obtained using the estimated volume of combusted gas and the available emission factors. Combining the estimate of current landfill gas volume that is combusted (4.7 billion m^3/yr) with the emission factor of 1.4 ng I-TEQ_{DF}/m^3 of flare-combusted gas yields an annual emission estimate of 6.6 g I-TEQ_{DF}. This estimate should be regarded as a preliminary indication of possible emissions from this source; further testing is needed to confirm the true magnitude of those emissions.

6.2. ACCIDENTAL FIRES

Accidental fires in buildings and vehicles are uncontrolled combustion processes that, because of poor combustion conditions, typically result in relatively high emissions of incomplete combustion products (Bremmer et al., 1994). The incomplete combustion products can include CDDs and CDFs. Polyvinyl chloride (PVC) building materials and furnishings, chloroparaffin-containing textiles and paints, and other chlorinated organic compound–containing materials appear to be the primary sources of the chlorine (Rotard,

1993). Although the results of several studies demonstrate the presence of CDD/CDF concentrations in soot deposits and residual ash from such fires, few direct measurements of CDD/CDFs in the fumes or smoke of fires have been reported. The results of some of those studies are described below, followed by an evaluation of the available data.

6.2.1. Soot and Ash Studies

Christmann et al. (1989b) analyzed the soot formed during combustion and pyrolysis of pure PVC and PVC cable sheathings in simple laboratory experiments designed to mimic the conditions of fires. For the combustion experiments, 2 grams of a PVC sample were incinerated with a laboratory gas burner. The combustion products were collected on the inner walls of a cooled gas funnel placed above the sample. For the pyrolysis experiments, about 50 mg of the sample were placed in a quartz tube and heated to about 950°C for 10 minutes in either an air atmosphere or a nitrogen atmosphere. The combustion experiments yielded CDD/CDF concentrations in soot of 110 μg I-TEQ$_{DF}$/kg for a low-molecular-weight PVC, 450 μg I-TEQ$_{DF}$/kg for a high molecular weight PVC, and 270 μg I-TEQ$_{DF}$/kg for PVC cable. The pyrolysis experiments in the air atmosphere yielded lower CDD/CDF concentrations in soot: 24.4 μg I-TEQ$_{DF}$/kg for a low-molecular-weight PVC, 18.7 μg I-TEQ$_{DF}$/kg for a high-molecular-weight PVC, and up to 41 μg I-TEQ$_{DF}$/kg for PVC cable. In general, CDFs were predominantly formed over CDDs. The lower chlorinated CDF congeners were dominant in the combustion experiments; however, the HpCDF and OCDF congeners were dominant in the pyrolysis experiments. No CDD/CDFs were detected in pyrolysis experiments under a nitrogen atmosphere. Also, no CDD/CDFs were detected when chlorine-free polyethylene samples were subjected to the same combustion and pyrolysis conditions.

Deutsch and Goldfarb (1988) reported finding CDD/CDF concentrations ranging from 0.04 to 6.6 μg/kg in soot samples collected after a 1986 fire in a State University of New York lecture hall. The fire consumed or melted plastic furnishings, cleaning products containing chlorine, wood, and paper.

Funcke et al. (1988; as reported in Bremmer et al., 1994, and Rotard, 1993) analyzed 200 ash and soot samples from sites of accidental fires in which PVC was involved. CDD/CDFs were detected in more than 90 percent of the samples at concentrations in the ng I-TEQ$_{DF}$/kg to μg I-TEQ$_{DF}$/kg range. Fires involving the combustion

of materials containing relatively large amounts of PVC and other chlorinated organic substances resulted in the highest levels of CDD/CDFs, with CDD/CDF concentrations ranging from 0.2 to 110 μg I-TEQ$_{DF}$/kg of residue.

Thiesen et al. (1989) analyzed residues from surfaces of PVC-containing materials that were partially burned during accidental fires at sites in Germany that manufactured or stored plastics. CDD/CDF concentrations in residues were reported as 0.5 μg I-TEQ$_{DF}$/kg for soft PVC, 4.6 μg I-TEQ$_{DF}$/kg for PVC fibers, and 28.3 μg I-TEQ$_{DF}$/kg for a hard PVC. The ratio of total CDFs to total CDDs in the three samples ranged from 4:1 to 7:1. The dominant 2,3,7,8-substituted CDF and CDD congeners in all three samples were 1,2,3,4,6,7,8-HpCDF and 1,2,3,4,6,7,8-HpCDD.

Following an accidental fire at a Swedish carpet factory in 1987, 200 metric tons of PVC and 500 metric tons of PVC-containing carpet burned. Marklund et al. (1989) analyzed snow samples within 1,500 meters downwind from the fire site and found CDD/CDF concentrations in the top 2 cm ranging from 0.32 μg I-TEQ$_{DF}$/m^2 at 10 meters of the site to 0.01 μg I-TEQ$_{DF}$/m^2 at 1,500 meters downwind of the site. Because of an atmospheric inversion and very light wind at the time of the fire, the smoke from the fire remained close to the ground. The soot deposited onto the snow was thus assumed to be representative of the soot generated and released from the fire. Wipe samples of soot from interior posts of the plant (5 and 20 meters from the fire) contained EADON TEQ concentrations of 0.18 and 0.05 μg/m^2, respectively. On the basis of these deposition measurements, Marklund et al. (1989) estimated the total CDD/CDF emission from the fire to be less than 3 mg I-TEQ$_{DF}$.

Carroll (1996) estimated a soot-associated CDD/CDF emission factor (i.e., not including volatile emissions) of 28 to 138 ng I-TEQ$_{DF}$/kg of PVC burned for the Swedish carpet factory fire using the following assumptions: (1) the PVC carpet backing was one-half the weight of the carpet, (2) the carpet backing contained 30 percent by weight PVC resin, and (3) 20 to 100 percent of the PVC and PVC carpet backing present in the warehouse actually burned. Carroll (1996) also estimated a similar soot-associated emission factor (48 to 240 ng I-TEQ$_{DF}$/kg of PVC burned) for a fire at a plastics recycling facility in Lengerich, Germany. Carroll (1996) used the results of wipe samples collected at downwind distances of up to 6,300 meters from the fire to estimate the emission factor.

Fiedler et al. (1993) presented a case study of CDD/CDF contamination and associated remedial actions taken at a kindergarten in Germany following a fire, that destroyed parts of the roof, windows, and furnishings. Soot collected from the building contained CDD/CDFs at a concentration of 45 μg I-TEQ$_{DF}$/kg (or 15 μg I-TEQ$_{DF}$/m^2). Fiedler et al. (1993) attributed the CDD/CDFs detected to the combustion of plastic and wooden toys, floors, and furnishings; however, no information was provided on the quantities of those materials.

Fiedler and Lindert (1998) presented results of soot sampling following a serious fire at Düsseldorf Airport in Germany. Polystyrene sheets and PVC-coated cables were involved in the fire, together with PCB-containing condensers (bulbs). Surface wipe samples contained up to 0.33 μg I-TEQ$_{DF}$/m^2. Concentrations in soot ranged from 7 to 130 μg I-TEQ$_{DF}$/kg. Concentrations of BDD/BDFs were detected in soot at concentrations as high as 0.9 mg/kg soot.

Wichmann et al. (1993, 1995) measured the CDD/CDF content of ash and debris and deposited surface residues that resulted from experimental test burns of two cars (a 1974 Ford Taurus and a 1988 Renault Espace), one subway car, and one railway coach in a tunnel in Germany. On the basis of measurements obtained from sampled ash and debris and from soot collectors placed at regular intervals up to 420 meters downwind of the burn site, the total amounts of CDD/CDF in the ash/debris and tunnel surface residues from each vehicle burn experiment were estimated as follows: 1974 model car—0.044 mg I-TEQ$_{DF}$; 1988 model car—0.052 mg I-TEQ$_{DF}$; subway car—2.6 mg I-TEQ$_{DF}$; and railway coach—10.3 mg I-TEQ$_{DF}$. For each vehicle burn experiment, the mass of TEQ in tunnel surface residue exceeded the mass in ash and debris; 73 to 89 percent were accounted for by the tunnel surface residues and 11 to 27 percent by ash and debris. The average CDD/CDF content of the ash and debris from each experimental burn was as follows: new car—0.14 μg I-TEQ$_{DF}$/kg; old car—0.30 μg I-TEQ$_{DF}$/kg; subway car—3.1 μg I-TEQ$_{DF}$/kg; and railway coach—5.1 μg I-TEQ$_{DF}$/kg.

6.2.2. Fume and Smoke Studies

Merk et al. (1995) collected fume and smoke generated during the burning of 400 kg of wood and 40 kg of PVC in a building (4,500 m^3 volume) over a 45-minute period. The sampling device consisted of dual glass fiber filters to collect particles greater than 0.5

μm, followed by a polyurethane foam filter to collect vapor phase CDD/CDFs. The particulate phase and gas phase showed the same congener pattern, decreasing concentration with increasing degree of chlorination, thus indicating no preferential sorption of higher chlorinated congeners to smoke particulates. However, the CDD/CDF found in the gas phase (about 5 ng I-TEQ_{DF}/m^3) accounted for more than 90 percent of the detected CDD/CDFs. Merk et al. (1995) also reported that the soot deposited from this fire onto a 1 m^2 aluminum sheet resulted in surface contamination of 0.050 μg I-TEQ_{DF}/m^2. Although it was stated in Merk et al. (1995) that the building was 'closed,' subsequent communication with one of the coauthors (Schramm, 1998) clarified that a 'gas cleaning' system was in operation during the testing. Because a ventilation system was in operation during the testing, there was likely some loss of vapor phase CDD/CDFs from the hall. Therefore, the deposits (from particulate deposition and vapor phase condensation) on the test aluminum plate may not reflect total CDD/CDF formation during the fire.

Dyke and Coleman (1995) reported a fourfold increase in CDD/CDF TEQ concentrations in the ambient air during "bonfire" night in Oxford, England. Bonfire night (November 5) is an annual event in England during which it is customary to set off fireworks and have bonfires to commemorate a failed plot to overthrow the king in 1605. Air concentrations before and after bonfire night ranged from 0.15 to 0.17 pg I-TEQ_{DF}/m^3. The air concentration during the bonfire night was 0.65 pg I-TEQ_{DF}/m^3. The dominant congeners in all samples were the hepta- and octa-CDDs. The study was not designed to collect data that would enable calculation of an emission rate nor to differentiate the relative importance of the various materials combusted. However, the results do indicate that open burning of materials likely to be combusted in accidental fires (with the exception of fireworks) results in the release of CDDs and CDFs.

6.2.3. Data Evaluation

Structural Fires — The limited data available on structural fires were judged inadequate for developing national emission estimates that could be included in the national inventory. This conclusion was also reached in national emission inventories developed for The Netherlands (Bremmer et al., 1994) and the United Kingdom (UK Department of the Environment, 1995). Most cited studies involved situations (i.e., field and laboratory) where relatively high loadings of PVC or plastics were combusted. The effects of different

mixes of combusted materials, oxygen supplies, building configurations, durations of burn, and so forth, likely to be found in accidental fires cannot be accounted for by the factors that can be derived from these studies. Also, most of the studies addressed only soot or ash residues and did not address potential volatile emissions of CDD/CDFs which, according to Merk et al. (1995), may represent 90 percent of the CDD/CDFs generated during burning of PVC.

Two recent reports (Carroll, 1996; Thomas and Spiro, 1995) attempted to quantify CDD/CDF emissions from U.S. structural fires, and Lorenz et al. (1996) estimated emissions from structural fires in the Federal Republic of Germany. The estimates derived in these three studies are presented below, following a brief summary of the number and types of accidental fires reported annually in the United States.

In 1995, approximately 574,000 structural fires were reported in the United States. Of these, 426,000 were reported for residential structures, including 320,000 fires in 1–2 family units, 94,000 fires in apartments, and 12,000 fires in other residential settings. The remaining 148,000 structural fires were broken down as follows: 15,000—public assembly; 9,000—educational; 9,000—institutional; 29,000—stores and offices; 29,000—special structures; 39,000—storage; and 18,000—industry, utility, and defense. The latter two categories may be underreported as some incidents were handled by private fire brigades or fixed suppression systems, which do not report (U.S. DOC, 1997).

Carroll (1996) estimated the total CDD/CDF content of soot and ash generated from the 358,000 fires reported in U.S. DOC (1995a) for 1993 in 1–2 family unit residential structural fires. Carroll (1996) developed detailed estimates of the PVC content of typical homes, including plumbing, wiring, siding and windows, wallpaper, blinds and shades, and upholstery. Using statistical data on fire loss (i.e., dollar value) provided the typical loss per recorded fire (9.5 percent of value) which Carroll assumed also represented the typical percentage of PVC burned. Extrapolating to all 358,000 1–2 family unit fires yielded an annual mass of 2,470 metric tons of PVC burned. Carroll (1996) then developed TEQ emission factors from the results of Thiesen et al. (1989) and Marklund et al. (1989). The estimated CDD/CDF content ranged from 0.47 to 22.8 g I-TEQ_{DF} with 0.07 to 8.6 g I-TEQ_{DF} in soot and 0.4 to 14.2 g I-TEQ_{DF} in ash. Carroll derived a soot emission factor (i.e., grams of soot produced per gram of PVC combusted) from his assumptions regarding the surface area of the soot collection funnel used by Christmann et al. (1989a) and the soot

deposition rate on that funnel. Carroll then applied these I-TEQ_{DF} emission factors to the estimated 2,470 metric tons of PVC burned annually in 1–2 family unit residential fires to obtain estimates of the annual mass of TEQ that would be found in the soot and ash of residential fires (i.e., 0.48 to 22.8 g I-TEQ_{DF}/yr). The average emission per fire is thus 1.3 to 64 μg I-TEQ_{DF}.

Thomas and Spiro (1995) estimated that 20 g of I-TEQ_{DF} may be released annually to air from structural fires. This estimate assumed an emission factor of 4 ng I-TEQ_{DF}/kg of material combusted (i.e., the emission rate for "poorly controlled" wood combustion), an assumed material combustion factor of 6,800 kg/fire, and 688,000 structural fires per year. The average emission per fire is thus 29 μg I-TEQ_{DF}.

Lorenz et al. (1996) estimated annual generation of CDD/CDF TEQs in the Federal Republic of Germany using data on the number of residential and industrial/commercial structural fires coupled with data on CDD/CDF content in soot and ash residues remaining after fires. The potential annual I-TEQ_{DF} generation was estimated to be 78 to 212 grams.

Although, as stated above, the available data were judged to be inadequate to support development of an emission estimate for the national inventory, a preliminary estimate of the potential magnitude of TEQ emissions can be obtained using the estimates of Carroll (1996) and Thomas and Spiro (1995), that annual releases are about 20 g I-TEQ_{DF}.

There is very low confidence in these estimated emissions because of the numerous assumptions employed in their derivation. If the conclusion of Merk et al. (1995) is assumed to be correct, that 90 percent of the CDD/CDFs formed in fires are in the gaseous phase rather than particulate phase (i.e., greater than 0.5 μm diameter), and it is also assumed that the estimates of Carroll (1996) and of Thomas and Spiro (1995) do not totally account for volatile emissions, then the total CDD/CDF emissions estimated by Carroll (1996) and by Thomas and Spiro (1995) may be underestimates. Further testing is needed to confirm the true magnitude of these releases.

Vehicle Fires—The limited data available on vehicle fires were judged inadequate for developing national emission estimates that could be included in the national inventory. However, a preliminary estimate of the range of potential CDD/CDF emissions that may result from vehicle fires can be calculated using the results reported by Wichmann et al. (1993, 1995) for controlled vehicle fires in a tunnel (0.044 mg I-TEQ_{DF} for an old car to 2.6

mg I-TEQ_{DF} for a subway car). Although Wichmann et al. (1993; 1995) did not measure volatile CDD/CDFs (which were reported by Merk et al. (1995) to account for the majority of CDD/CDFs formed during a fire), the study was conducted in a tunnel, and it is likely that a significant fraction of the volatile CDD/CDFs sorbed to tunnel and collector surfaces and were thus measured as surface residues. In 1995, approximately 406,000 vehicle fires were reported in the United States (U.S. DOC, 1997). If it is assumed that 99 percent of those involved cars and trucks (i.e., the approximate percentage of all U.S. motor vehicles that are in-service cars and trucks; U.S. DOC, 1995a), and that the applicable emission rate is 0.044 mg I-TEQ_{DF} per incident, then the annual TEQ formation is 17.7 g I-TEQ_{DF}. The emission factor of 2.6 mg I-TEQ_{DF}/fire is assumed to be applicable to the remaining 1 percent of vehicle fires, thus yielding an emission of 10.6 g I-TEQ_{DF}/yr. The total TEQ annual emission is roughly estimated to be 28.3 g I-TEQ_{DF}/yr. This estimate should be regarded as a preliminary indication of possible emissions from this source category; further testing is needed to confirm the true magnitude of these emissions.

6.3. LANDFILL FIRES

In the late 1980s, two serious fires occurred in landfills near Stockholm, Sweden. The first involved a fire in a large pile of refuse-derived fuel. Using measurements of chlorobenzenes in the air emissions, it was estimated that 50 to 100 kg of chlorobenzenes were released. CDD/CDF emissions were estimated to be several tens of grams, on the assumption that the ratio of CDD/CDFs to chlorobenzenes in landfill fire emissions is similar to the ratio observed in stack gases of municipal waste incinerators. In connection with the second fire, which occurred at a large conventional landfill, birch leaves were collected from trees close to the fire and at distances up to 2 km downwind of the fire, as well as from nearby areas not affected by smoke from the fire. The discharge of CDD/CDF necessary to cause the CDD/CDF concentrations measured on the leaves was estimated to be several tens of grams (Persson and Bergström, 1991).

In response to these incidents, Persson and Bergström (1991) measured CDD/CDF emissions from experimental fires designed to simulate surface landfill fires and deep landfill fires. The experiments used 9-month-old domestic waste. The tests showed no significant difference in CDD/CDF content of the fire gas produced by the simulated surface and deep fires. The average CDD/CDF emission rate was reported to be 1 μg Nordic TEQ/kg of

waste burned. Persson and Bergström (1991) and Bergström and Björner (1992) estimated annual CDD/CDF Nordic TEQ emissions in Sweden from landfill fires to be 35 grams. The estimate was based on the emission rate of 1 μg Nordic TEQ/kg waste burned, an assumed average density of landfill waste of 700 kg/m^3, an assumed waste burn of 150 m^3 for each surface landfill fire (167 fires in Sweden per year), and an assumed waste burn of 500 m^3 for each deep landfill fire (50 fires in Sweden per year). The estimates of waste burn mass for each type of fire were the average values obtained from a survey of 62 surface fires and 25 deep fires. The estimated number of fires per year was based on the results of a survey of all Swedish municipalities for fires reported during the years 1988 and 1989. In 1991, Sweden had an estimated 400 municipal landfills (Persson and Bergström, 1991).

Ruokojärvi et al. (1995) measured the ambient air concentrations of CDD/CDF in the vicinity of real and experimental landfill fires in Finland. The most abundant toxic congeners were the hepta- and octa-CDDs and the penta-, hepta-, and octa-CDFs. The highest contributions to the measured TEQ were made by 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF. In Finland, annual CDD/CDF emissions from landfill fires are estimated to be 50–70 g Nordic TEQ (Aittola, 1993, as reported by Ruokojärvi et al., 1995).

Although no U.S. monitoring studies are available, an emission factor similar to the Swedish emission factor would be expected in the United States, because the contents of the municipal waste are expected to be similar between the United States and Sweden. However, because no data could be located on characterization of landfill fires in the United States (i.e., number, type, mass of waste involved), the limited data available were judged inadequate for developing national emission estimates that could be included in the national inventory. However, a preliminary estimate of the potential magnitude of TEQ emissions associated with landfill fires in the United States can be obtained by assuming a direct correlation of emissions to population size for the United States and Sweden or by assuming a direct correlation between emissions and the number of landfills in each country. Both countries are Western, industrialized countries. Although the per capita waste generation rate in the United States is nearly 1.5 times that of Sweden, the composition of municipal waste and the fraction of municipal waste disposed of in landfills in the two countries are nearly identical (U.S. EPA, 1996b). The 1995 population of Sweden is 8,822,000 (U.S. DOC, 1995a). Thus, the per capita landfill fire–associated Nordic TEQ emission factor is 4.0 μg TEQ/person/year (i.e., 35 grams/8,822,000 people).

Because congener-specific results were not provided in Persson and Bergström (1991) and Bergström and Björner (1992), it was not possible to derive emission factors in units of I-TEQ_{DF} or TEQ_{DF}-WHO_{98}. Applying this factor to the U.S. population (263,814,000) (U.S. DOC, 1995a) results in an estimated annual emission of 1,050 g of TEQ. This estimate should be regarded as a preliminary indication of possible emissions from this source category; further testing is needed to confirm the true magnitude of these emissions. An annual emission of similar size is obtained if it is assumed that the ratio of annual TEQ emissions to number of landfills in Sweden, 87.5 mg TEQ/landfill (i.e., 35 grams/400 landfills), is applicable to the United States, which has 3,558 landfills (U.S. EPA, 1996b). The resulting annual emission estimate is 311 g TEQ/yr.

6.4. FOREST AND BRUSH FIRES

Because CDD/CDFs have been detected both in the soot from residential wood burning (Bumb et al., 1980; Nestrick and Lamparski, 1982, 1983; Bacher et al., 1992), and in the flue gases from residential wood burning (Schatowitz et al., 1993; Vickelsoe et al., 1993), it is reasonable to presume that wood burned in forest and brush fires may also be a source of CDD/CDFs (Section 4.2 contains details on these studies).

Only one study could be found that reported direct measurements of CDD/CDFs in the emissions from forest fires. This study, by Tashiro et al. (1990), reported detection of total CDD/CDFs in air at levels ranging from about 15 to 400 pg/m^3. The samples were collected from fixed collectors located 10 meters above the ground and from aircraft flying through the smoke. Background samples collected before and after the tests indicated negligible levels in the atmosphere. These results were presented in a preliminary report; however, no firm conclusions were drawn about whether forest fires are a CDD/CDF source. The final report on this study, Clement and Tashiro (1991), reported total CDD/CDF levels in the smoke of about 20 pg/m^3. The authors concluded that CDD/CDFs are emitted during forest fires but recognized that some portion of these emissions could represent resuspension from residues deposited on leaves rather than newly formed CDD/CDFs.

Although not designed to directly assess whether CDD/CDFs are formed during brush fires, Buckland et al. (1994) measured the CDD/CDF levels in soil samples from both burnt and unburnt areas in national parks in New Zealand 6 weeks after large-scale brush

fires. Four surface soil cores (2 cm depth) were collected and composited from each of three burnt and three unburnt areas. Survey results indicated that brush fires did not have a major impact on the CDD/CDF levels in soil. The I-TEQ_{DF} contents in soil sample composites of the three unburnt areas were 3.0 ng/kg, 8.7 ng/kg, and 10.0 ng/kg. The I-TEQ_{DF} contents in the soil sample composites of three burnt areas were 2.2 ng/kg, 3.1 ng/kg, and 36.8 ng/kg. Total CDD/CDF contents ranged from 1,050 to 7,700 ng/kg in the unburnt area soil samples and from 1,310 to 27,800 ng/kg in the burnt area soil samples. OCDD accounted for 94 to 97 percent of the total CDD/CDF content in all samples.

Similarly, a survey of controlled straw-field burning in the United Kingdom (Walsh et al., 1994) indicated that the straw burning did not increase CDD/CDF burden in the soil; however, a change in congener distribution was observed. Soils from three fields were sampled immediately before and after burning, along with ash from the fire. The mean I-TEQ_{DF} concentrations in the preburn soil, postburn soil, and ash were 1.79 ng/kg, 1.72 ng/kg, and 1.81 ng/kg, respectively. Concentrations of 2,3,7,8-TCDF were lower in the postburn soils than in the preburn soils. Conversely, the concentrations of OCDD were higher in the postburn soils indicating possible formation of OCDD during the combustion process.

Van Oostdam and Ward (1995) reported finding no detectable levels of 2,3,7,8-substituted CDD/CDFs in three soil samples and four ash samples following a forest fire in British Columbia. The detection limits on a congener-specific basis (unweighted for TEQ) ranged from 1 to 2 ng/kg. Nondetected values were also reported by Van Oostdam and Ward (1995) for ashes at a slash and burn site; the soil contained about 0.05 ng I-TEQ_{DF}/kg, whereas background soil contained about 0.02 ng I-TEQ_{DF}/kg.

The concentrations presented by Clement and Tashiro (1991) cannot accurately be converted to an emission factor, because the corresponding rates of combustion gas production and wood consumption are not known. As a result, three alternative approaches were considered to develop an emission factor.

Soot-Based Approach—This approach assumes that the levels of CDD/CDFs in chimney soot are representative of the CDD/CDFs in emissions. The CDD/CDF emission factor is calculated as the product of the CDD/CDF concentration in soot and the total particulate emission factor. This calculation involves first assuming that the CDD/CDF

levels measured in chimney soot (720 ng I-TEQ_{DF}/kg) by Bacher et al. (1992) are representative of the CDD/CDF concentrations of particles emitted during forest fires. Second, the total particulate generation factor must be estimated. Ward et al. (1976) estimated the national average particulate emission factor for wildfires as 150 lb/ton biomass dry weight using primarily data for head fires. Ward et al. (1993) estimated the national average particulate emission factor for prescribed burning as 50 lb/ton biomass dry weight. Combining the total particulate generation rates with the I-TEQ_{DF} level in soot results in emission factor estimates of 54 ng of I-TEQ_{DF} and 18 ng of I-TEQ_{DF}/kg of biomass burned in wildfires and prescribed burns, respectively. These estimated factors are likely to be overestimates, because the levels of CDD/CDF measured in chimney soot by Bacher et al. (1992) may represent the accumulation and enrichment of CDD/CDFs measured in chimney soot over time, leading to much higher assumed levels than what is actually on emitted particles.

Carbon Monoxide (CO) Approach—Carbon monoxide is a general indicator of the efficiency of combustion, and the emission factors of many emission products can be correlated to the CO emission factor. The Schatowitz et al. (1993) data for emissions during natural wood burning in open stoves suggest an emission factor of 10 μg I-TEQ_{DF}/kg of CO. Combining this factor with the CO emission factor during forest fires (roughly 0.1 kg CO/kg of biomass, Ward et al., 1993) yields an emission factor of 1,000 ng I-TEQ_{DF}/kg biomass. This factor is higher than the soot-based factor discussed above, which is itself considered to be an overestimate. In addition, although the formation kinetics of CDD/CDF during combustion are not well understood, CDD/CDF emissions have not been shown to correlate well with CO emissions from other combustion sources. (See Chapter 2.)

Wood Stove Approach—This approach assumes that the emission factor for residential wood burning (using natural wood and open door, i.e., uncontrolled draft) applies to forest fires. As discussed in Section 4.2.1, this approach suggests an emission factor of about 2 ng I-TEQ_{DF}/kg of wood burned. This value appears more reasonable than the factors suggested by the soot and CO approaches because it is based on direct measurement of CDD/CDFs from combustion of wood rather than indirect techniques. However, forest fire conditions differ significantly from combustion conditions in wood

stoves. For example, forest fire combustion does not occur in an enclosed chamber, and the biomass consumed in forest fires is usually green and includes underbrush, leaves, and grass. Given these differences and the uncertainties about the formation kinetics of CDD/CDF during combustion, it is difficult to determine whether CDD/CDF emissions would be higher or lower from forest fires than from wood stoves. Thus, although an emission factor of 2 ng I-TEQ_{DF}/kg appears to be the best estimate that can be made currently, it must be considered highly uncertain.

The limited emission factor data available and the degree of confidence in the three approaches evaluated to derive an emission factor were judged inadequate for developing national emission estimates that could be included in the national inventory. However, a preliminary estimate of the potential annual TEQ release associated with forest and brush fires can be obtained using estimates of the biomass burned annually in wildfire and prescribed burns and the emission factor used for wood stoves (2 ng I-TEQ_{DF}/kg of biomass). According to the Council on Environmental Quality's 25th Annual Report (CEQ, 1997), 5 million acres of forest were lost to wildfires in 1987 and 7 million acres were lost in 1995. Estimates of the acreage consumed annually during prescribed burns are not readily available for the reference years 1995 and 1997. An estimated 5.1 million acres of biomass were burned in 1989 during prescribed burns (Ward et al., 1993). Prescribed burning, also known as managed or controlled burning, is used as a forest, range, and wetland management tool conducted under prescribed weather and fuel conditions. This value of 5.1 million acres is assumed to be an appropriate value to use for reference years 1987 and 1995.

Combining these acreage estimates with biomass consumption rates of 9.43 metric tons/acre in areas consumed by wildfires (Ward et al., 1976) and 7.44 metric tons/acre in areas consumed in prescribed burns (Ward et al., 1993) indicates that 47 million metric tons of biomass were consumed by wildfires in 1987, 66 million metric tons were consumed by wildfires in 1995, and 38 million metric tons were consumed by prescribed burns in 1987 and 1995.

Combining the emission factor developed using the wood stove approach (2 ng I-TEQ_{DF}/kg biomass) with the amount of biomass consumed annually in wildfires and prescribed fires (total of 85 million metric tons in 1987 and 104 million metric tons in 1995) yields I-TEQ_{DF} annual emission estimates of 170 g in 1987 and 208 g in 1995.

These estimates should be regarded as preliminary indications of possible emissions from this source; further testing is needed to confirm the true magnitude of emissions.

6.5 BACKYARD BARREL BURNING

In many rural areas of the United States, disposal of residential solid waste may take place via open backyard burning in barrels or similar homemade devices. Although no national statistics on the prevalence of this practice have been reported, the results of a telephone survey conducted in the early 1990s of residents in five central Illinois counties indicate that about 40 percent of the residents in a typical rural Illinois county burn household waste. The survey also found that, on average, those households that burn waste dispose of approximately 63 percent of their household waste by burning it in barrels (Two Rivers Region Council of Public Officials and Patrick Engineering, 1994).

Similar results were recently obtained in a survey conducted by Zenith Research Group, Inc. for the Western Lake Superior Sanitary District of Minnesota (Zenith, 2000). This survey of 760 residents of selected portions of Northwest Wisconsin and Northeast Minnesota addressed, in part, use of burn barrels or other devices to burn household garbage or other materials. The survey found that 71 percent of the respondents indicated their residence currently had garbage hauling service. Of those respondents lacking a garbage hauling service, 92 percent said they currently used a nearby garbage disposal site. However, among all respondents, 27.5 percent admitted they currently use a burn barrel or other device to burn household garbage or other materials. Of these respondents who admitted burning, 39 percent indicated they burn at least weekly and 30 percent indicated they burned once or twice monthly.

The low combustion temperatures and oxygen-starved conditions associated with these devices may result in incomplete combustion and increased pollutant emissions. In 1997, EPA's Control Technology Center, in cooperation with the New York State Departments of Health (NYSDOH) and Environmental Conservation (NYSDEC), conducted an initial study to examine, characterize, and quantify emissions from the simulated open burning of household waste materials in barrels (Lemieux, 1997). A representative waste to be burned was prepared based on the typical percentages of various waste materials disposed of by New York State residents (i.e., nonavid recyclers); hazardous wastes (i.e., chemicals, paints, oils, etc.) were not included in the test waste. A variety of compounds,

including CDD/CDFs, were measured in the emissions from two simulated open burnings of this "baseline" waste.

Combustion studies were subsequently performed by EPA to provide additional "baseline" waste tests and to provide an initial indication of the impact of limited variation in waste composition and combustion conditions on CDD/CDF emissions from a simulated domestic backyard barrel burn of 6.8 kg of unshredded household waste (Gullet et al., 1999; 2000a; 2000b; Lemieux et al., 2000; Lemieux, 2000).

The results of seven "baseline" waste tests were reported in these EPA studies. These tests exhibited variation in the emissions of CDD/CDFs with a 1-2 order of magnitude spread between the lowest and highest values for individual congeners, congener groups, total CDD/CDFs, and TEQ values. The average TEQ emission factor for the seven wastes was 72.8 ng I-TEQ_{DF}/kg of waste burned (setting not detected values equal to zero) and 73.7 ng I-TEQ_{DF}/kg (setting not detected values equal to one-half the detection limit). The corresponding TEQ_{DF}-WHO_{98} values were 76.8 and 77.7 ng TEQ_{DF}-WHO_{98}/kg. Table 6-2 presents the average congener and congener group results for these tests.

Variation from the baseline waste chlorine content (0.2 percent by weight PVC) included testing at three different PVC levels (0, 1.0, and 7.5 percent by weight PVC). The average emissions from the 0, 1.0, and 7.5 percent PVC were, respectively, 14, 201, and 4,916 ng I-TEQ_{DF}/kg. Two tests using waste impregnated with inorganic chloride (i.e., $CaCl_2$) at a 7.5 percent by weight level (and no PVC) averaged 734 ng I-TEQ_{DF}/kg. Qualitative comparisons suggest that the tests with higher Cl, via PVC or $CaCl_2$, resulted in substantial increase in TEQ emissions.

Other variations in baseline waste composition included conducting one test with compressed waste, one test with a double load of waste, and one test in which some of the waste paper was wetted to simulate high moisture burns. These tests resulted in a higher mean TEQ emission factor (534 ng I-TEQ_{DF}) than that of the baseline runs.

Several waste combustion variables were studied such as average temperatures at prescribed barrel heights, duration that temperatures were within the favorable temperature range for CDD/CDF formation, and measurement of CO, CO_2, O_2, PM, and HCl. Statistical analyses of the results indicated that an interactive term, the product of the CO emissions and the temperature in the uppermost portion of the barrel, and CO emissions were the

best predictors of TEQ variation. However, the wide variability in test results (i.e., from less than 10 to more than 6,000 ng I-TEQ_{DF}/kg) also indicates that a high degree of CDD/CDF emission variation can be expected due to factors, such as waste orientation, that are not wholly related to waste composition or burning practice.

The limited emission factor and activity level data available for developing national emission estimates that could be included in the national inventory were assigned low confidence ratings. The number of households nationwide burning waste in barrels and the total amount and variability of burned waste can only be roughly estimated, and the representativeness of the trash and burning conditions used in the baseline experiments to conditions nationwide is uncertain. Combining the emission factors of 72.8 ng I-TEQ_{DF}/kg of waste burned and 76.8 ng TEQ_{DF}-WHO_{98}/kg with the following information and assumptions allows estimates to be made of the potential magnitude of national CDD/CDF TEQ emissions from backyard household trash burning.

- Of the rural population in the United States, 40 percent are assumed to burn their household waste in a barrel (Two Rivers Region Council of Public Officials and Patrick Engineering, 1994).

- On average, each U.S. citizen generates 3.72 pounds of solid waste (excluding yard waste) per day (or 616 kg/person-yr) (U.S. EPA, 1996b).

- On average, in households that dispose of household waste by burning, approximately 63 percent of waste generated is burned (i.e., 63 percent of 616 kg/person-yr = 388 kg/person-year) (Two Rivers Region Council of Public Officials and Patrick Engineering, 1994).

- In 1994 (used for 1995 reference year), 52.7 million people lived in nonmetropolitan areas. In 1990 (used for 1987 reference year), 50.7 million people lived in nonmetropolitan areas (U.S. DOC, 1997).

Annual nationwide TEQ emissions were calculated using Equation 6-1.

$$E_{TEQ} = EF_{TEQ} \times P \times F \times W \qquad \text{(Eqn. 6-1)}$$

where:

E_{TEQ} = Annual TEQ_{DF} emissions (g/yr)
EF_{TEQ} = TEQ_{DF} emission factor (g TEQ_{DF}/kg of waste)
P = Nonmetropolitan population of U.S. in reference year
F = Fraction of nonmetropolitan population assumedto burn household waste (0.4)

W = Mass of household waste burned per year on a per capita basis (388 kg/person-year)

Therefore, estimated nationwide emissions in 1995 and 1987 were 595 g I-TEQ_{DF} (628 g TEQ_{DF}-WHO_{98}) and 573 g I-TEQ_{DF} (604 g TEQ_{DF}-WHO_{98}), respectively.

6.6. UNCONTROLLED COMBUSTION OF POLYCHLORINATED BIPHENYLS (PCBs)

The accidental combustion of PCB-containing electrical equipment or intentional combustion of PCBs in incinerators and boilers not approved for PCB burning (40 CFR 761) may produce CDDs and CDFs. At elevated temperatures, such as in transformer fires, PCBs can undergo reactions to form CDF and other by-products. More than 30 accidental fires and explosions involving PCB transformers and capacitors in the United States and Scandinavia, which involved the combustion of PCBs and the generation of CDDs and CDFs, have been documented (Hutzinger and Fiedler, 1991b; O'Keefe and Smith, 1989; Williams et al., 1985). For example, analyses of soot samples from a Binghamton, New York, office building fire detected 20 μg/g of total CDDs (0.6 to 2.8 μg/g of 2,3,7,8-TCDD) and 765 to 2,160 μg/g of total CDFs with 12 to 270 μg/g of 2,3,7,8-TCDF. At that site, the fire involved the combustion of a mixture containing PCBs (65 percent) and chlorobenzene (35 percent). Laboratory analyses of soot samples from a PCB transformer fire, which occurred in Reims, France, indicated total CDD and CDF levels in the range of 4 to 58,000 ng/g and 45 to 81,000 ng/g, respectively.

Using a bench-scale thermal destruction system, Erickson et al. (1984) determined the optimum conditions for CDF formation to be 675°C, an excess oxygen concentration of 8 percent, and a residence time of 0.8 seconds or longer. Combusting mineral oil and silicone oil containing 5, 50, and 500 ppm of Aroclor 1254 at these conditions for 0.8 seconds yielded PCB to CDF conversion efficiencies as high as 4 percent. Up to 3 percent conversion efficiency was observed when an askarel (70 percent Aroclor 1260) was combusted under the same conditions.

The use of PCBs in new transformers in the United States is banned, and their use in existing transformers and capacitors is being phased out under regulations promulgated under the Toxic Substances Control Act (TSCA).

Because of the accidental nature of these incidents, the variation in duration and intensity of elevated temperatures, the variation in CDD/CDF content of residues, and

uncertainty regarding the amount of PCBs still in service in electrical equipment, EPA judged the available data inadequate for developing national emission estimates that could be included in the national inventory. However, Thomas and Spiro (1995) conservatively estimated that about 15 g of TEQ may be generated annually from fires in commercial and residential buildings each year. This estimate is based on the following assumptions: (1) the I-TEQ_{DF} emission rate is 20 μg/kg of PCB burned; (2) 74,000 metric tons of PCB are still in use in various electrical equipment; and (3) 1 percent of the in-use PCBs is burned during the course of structural fires annually.

6.7. VOLCANOES

To date, no studies demonstrating formation of CDD/CDFs by volcanoes have been published. Given the available information from the studies discussed below, volcanoes do not appear to be sources of CDD/CDF release to the environment.

Gribble (1994) summarized some of the existing information on the formation of chlorinated compounds by natural sources, including volcanoes. Gribble (1994) reported that several studies had demonstrated the presence of chlorofluorocarbons and simple halogenated aliphatic compounds (one and two carbon chain length) in volcanic gases. In addition, several chlorinated monoaromatic compounds as well as three PeCB congeners were reported as having been detected in the ash from the 1980 eruption of Mount St. Helens. Gribble hypothesized that the formation of these PCB compounds was the result of rapid, incomplete high-temperature combustion of chloride-containing plant material in the eruption zone. However, he presented no information indicating formation of CDD/CDFs by volcanoes.

Lamparski et al. (1990) analyzed groundfall ash samples collected at various distances and locations from Mount St. Helens following the eruption in 1980. The findings of this study indicate that volcanic particulate emissions were free of detectable PCBs and nearly free of detectable CDDs (0.8 ng/kg HpCDD detected) upon exiting the volcano and remained so throughout their period of deposition in the blast zone. However, upon transport through the atmosphere, measurable and increasing levels of CDDs and PCBs were detected in deposited ash as the ash passed from rural to urban environments. The authors hypothesized that CDDs and PCBs in the atmosphere became associated with the volcanic ash particulates through gas-phase sorption or particulate agglomeration.

Takizawa et al. (1994) sampled the dust fall from the active volcano, Fugendake, as well as the volcanic ash from the active volcano, Sakurajima, for CDD and CDF congener group concentrations. The study was not designed to determine whether the CDD/CDFs observed were formed by the volcanoes or were scavenged from the atmosphere by the falling dust and ash. The dust fall was collected for 1-month periods during July and October 1992; two samples of the volcanic ash were collected in 1992. The results of the sample analyses for 2,3,7,8-substituted CDDs and CDFs, presented in Table 6-3, show that no 2,3,7,8-substituted congeners with less than 7 chlorines were detected; however, Takizawa et al. (1994) reported that non-2,3,7,8-substituted congeners in the lower chlorinated congener groups were detected.

Table 6-1. CDD/CDF Emission Factors for a Landfill Flare

Congener/Congener Group	Mean Facility Emission Factor* (ng/m^3 gas combusted)
2,3,7,8-TCDD	0.018
1,2,3,7,8-PeCDD	0.092
1,2,3,4,7,8-HxCDD	0.074
1,2,3,6,7,8-HxCDD	0.074
1,2,3,7,8,9-HxCDD	0.259
1,2,3,4,6,7,8-HpCDD	0.755
OCDD	4.414
2,3,7,8-TCDF	14.074
1,2,3,7,8-PeCDF	0.385
2,3,4,7,8-PeCDF	1.136
1,2,3,4,7,8-HxCDF	1.455
1,2,3,6,7,8-HxCDF	0.422
1,2,3,7,8,9-HxCDF	0.110
2,3,4,6,7,8-HxCDF	0.681
1,2,3,4,6,7,8-HpCDF	1.215
1,2,3,4,7,8,9-HpCDF	0.073
OCDF	0.639
Total 2,3,7,8-CDD	5.686
Total 2,3,7,8-CDF	20.192
Total I-TEQ_{DF}	2.392
Total TEQ_{DF}-WHO_{98}	2.433
Total TCDD	NR
Total PeCDD	NR
Total HxCDD	NR
Total HpCDD	NR
Total OCDD	NR
Total TCDF	NR
Total PeCDF	NR
Total HxCDF	NR
Total HpCDF	NR
Total OCDF	NR
Total CDD/CDF	NR

* Assumes heat content of 1.86E + 07 J/m^3 for landfill gas (Federal Register, 1996a).
NR = not reported.

Source: CARB (1990d)

Table 6-2. CDD/CDF Air Emission Factors from Barrel Burning of Household Waste

Congener/Congener Group	Average Air Emission Factors [a] (ng/kg waste burned)	
	Nondetects Set to 1/2 Det. Limit	Nondetects Set to Zero
2,3,7,8-TCDD	3.4	2.7
1,2,3,7,8-PeCDD	8.2	8.1
1,2,3,4,7,8-HxCDD	6.6	6.4
1,2,3,6,7,8-HxCDD	9.9	9.7
1,2,3,7,8,9-HxCDD	19.1	19.0
1,2,3,4,6,7,8-HpCDD	39.8	39.8
OCDD	49.7	49.7
2,3,7,8-TCDF	45.6	45.6
1,2,3,7,8-PeCDF	37.2	37.2
2,3,4,7,8-PeCDF	65.2	65.2
1,2,3,4,7,8-HxCDF	113.8	113.8
1,2,3,6,7,8-HxCDF	38.5	38.5
2,3,4,6,7,8-HxCDF	61.9	61.9
1,2,3,7,8,9-HxCDF	3.0	2.5
1,2,3,4,6,7,8-HpCDF	128.6	124.4
1,2,3,4,7,8,9-HpCDF	14.6	15.0
OCDF	37.5	36.4
Total 2,3,7,8-CDD	136.6	135.4
Total 2,3,7,8-CDF	545.8	540.4
Total I-TEQ_{DF}	73.7	72.8
Total TEQ_{DF}-WHO_{98}	77.7	76.8
Total TCDD	413	413
Total PeCDD	281	281
Total HxCDD	221	221
Total HpCDD	105	105
Total OCDD	43	43
Total TCDF	1,880	1,880
Total PeCDF	1,021	1,021
Total HxCDF	492	492
Total HpCDF	169	169
Total OCDF	32	30
Total CDD/CDF	4,657	4,656

a Listed values are the arithmetic averages of seven tests for the congeners and the averages of five tests for the congener groups.

Source: Lemieux (2000); Gullett et al. (1999; 2000a; 2000b).

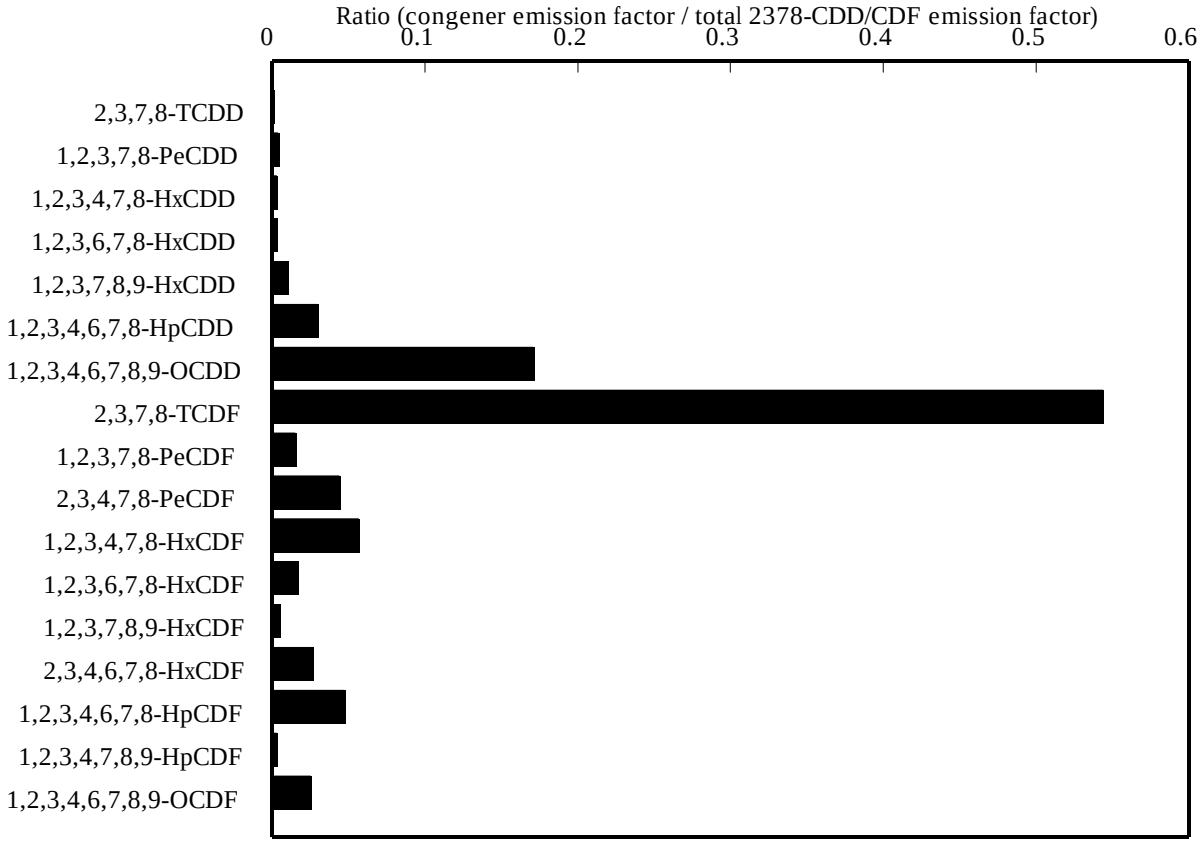
Table 6-3. CDD/CDF in Dust Fall and Ashes from Volcanoes

2,3,7,8-Substituted Congener Group	Dust Fall (mg/km^2/month)[a]		Volcanic Ash (ng/kg)[b]	
	July 1992	Oct. 1992	Ash No. 1	Ash No. 2
TCDD	< 0.5	< 0.5	< 0.1	< 0.1
PeCDD	< 0.5	< 0.5	< 0.1	< 0.1
HxCDD	< 0.5	< 0.5	< 0.1	< 0.1
HpCDD	9.2	5.2	2.5	1.8
OCDD	14	11	1.7	2.2
TCDF	< 0.5	< 0.5	< 0.1	< 0.1
PeCDF	< 0.5	< 0.5	< 0.1	< 0.1
HxCDF	< 0.5	< 0.5	< 0.1	< 0.1
HpCDF	1.9	2.8	1.2	1.2
OCDF	4.2	1.8	< 0.5	< 0.5

a Dust fall measured from the active volcano, Fugendake.

b Volcanic ash measured from active volcano, Sakurajima.

Source: Takizawa et al. (1994).



Source: CARB (1990d).

Figure 6-1. Congener Profile for Landfill Flare Air Emissions